added to a suspension of Cp_2ZrH_2 (0.88 g, 4 mmol) in benzene (10 mL), and the mixture was heated at 45 °C for 8 h. Black finely divided material was removed by filtration through Celite, and the filtrate was pumped down to a green yellow oil. The product could not be crystallized, but ^1H NMR spectra showed only one major component (>95%). ^1H NMR (benzene) δ 5.75 (s, 10, Cp), 1.5–1.1 (m, 4, CH_2Bu-*t*), 0.88 (s, 18, Me), 0.5–1.0 (m, 4, $ZrCH_2$).

(ii) A solution of $Cp_2Zr(CH_2CH_2Bu\text{-}t)_2$ (0.5 g, 1.3 mmol) was dissolved in toluene (20 mL) and stirred under H_2 (1 atm) attached to a gas buret (50 mL). After 2 days, most of the starting material was recovered.

(I) Hydrogenation of $Cp_2Zr(COCH_2\overline{CH(CH_2)_4C}H_2)Cl$ (5). $Cp_2Zr(CO\overline{CH(CH_2)_4C}H_2)Cl$ (**5**) (0.55 g, 1.4 mmol) was dissolved in toluene (20 mL). It failed to react with H_2 (92 atm) over 2 days at room temperature.

Acknowledgment. We acknowledge generous support for this work by the National Science Foundation (Grant No. CHE-79-00996). K.I.G. also acknowledges support from a University Travelling Scholarship from the Australian National University.

Registry No. 1a, 54634-15-0; **1b**, 80789-41-9; **1c**, 37343-38-7; **1d**, 12109-84-1; **1e**, 1291-45-8; **2a**, 69058-71-5; **2a′**, 67063-44-9; **2b**, 67077-97-8; **2b′**, 67660-04-2; **2c**, 80789-42-0; **2d**, 80789-43-1; **2e**, 67659-92-1; **3a**, 80789-44-2; **3a′**, 80789-45-3; **3b′**, 80789-46-4; **3c**, 80789-47-5; **3d**, 80789-48-6; **3e**, 80789-49-7; **4**, 69106-29-2; **5**, 71068-71-8; **6** (X = Cl), 80789-50-0; $Cp_2Zr(H)Cl$, 37342-97-5; $Cp_2Zr(D)Cl$, 80789-51-1; Cp_2ZrH_2, 37342-98-6; Cp_2ZrD_2, 80789-52-2; $Cp_2Zr(OPr\text{-}i)_2$, 78091-18-6; $Cp_2Zr(OCDMe_2)_2$, 80789-53-3; $(Cp_2ZrCl)_2O$, 12097-04-0; $Cp_2Zr(OCDMe_2)Cl$, 80789-54-4; $Cp_2Zr(CH_2CH_2Bu\text{-}t)_2$, 80789-55-5; 3,3-dimethyl-1-butene, 558-37-2; **6** (X = H), 80789-56-6.

Stereochemically Nonrigid Silanes, Germanes, and Stannanes. 9.[1] Chiral Silylcyclopentadienes and Related Compounds: Mechanistic and Stereochemical Definition of Fluxional Behavior

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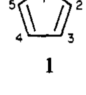
Abstract: Chirality at the Si atom in the silylcyclopentadienes $C_5H_5Si^*H(R)Cl$ (R = Me, *n*-Bu, or Me_3SiCH_2) and $C_5H_5Si^*H(i\text{-}Pr)(Me)$ results in anisochronicity among both pairs of olefinic ring nuclei ($C^{2,5}$ and $C^{3,4}$) in slow-limit ^{13}C NMR spectra. The larger diastereotopic shift is attributed in each system to that between those nuclei nearest to the chiral Si center, i.e., C^2 and C^5. With increasing temperature the pair of resonances so distinguished coalesces more rapidly with C^1 than do $C^{3,4}$, corresponding to fluxional characteristics qualitatively interpretable only in terms of a 1,2 pathway as the lowest energy rearrangement. This conclusion is supported by comparison with data simulated by using a five-site exchange program which (a) substantiate that 1,2 and 1,3 pathways are distinguishable and (b) yield $\Delta G^\ddagger$ = 61.3 (±1.3) and 59.8 (±2.7) kJ mol^{-1} for the Me_3SiCH_2 and *i*-Pr compounds, respectively. For the latter and in $C_5H_5M^*Me(i\text{-}Pr)(Ph)$ (M = Ge or Sn), ^1H and ^{13}C NMR spectra show magnetically nonequivalent methyl resonances for the *i*-Pr substituent; these diastereotopic shifts are temperature invariant, establishing that intramolecular metallotropic rearrangement occurs with retention of configuration at the migrating center M. Relationships with Woodward–Hoffmann [1,5] sigmatropic behavior are discussed.

Structural chemistry has been transformed by the advent of variable-temperature NMR spectroscopy, which has demonstrated that for certain kinds of molecules more than one configuration is thermally accessible at or near ambient temperature, resulting in facile intramolecular rearrangement between degenerate or nondegenerate states. The consequent dynamic stereochemistry has been termed *fluxional behavior*[3] where a structure alternates between two or more identical configurations (i.e., those having identical free energy), while we have called related systems[4] for which nonidentical configurations are accessed *"quasi-fluxional"*. The development of organometallic chemistry has presented a fascinating array of such molecules,[5] although important examples also exist which are strictly organic[3,6] or inorganic[7] in type.

Perhaps the class of compounds most closely identified with the initial recognition and subsequent characterization of fluxional behavior has been the *monohapto*cyclopentadienyl (η^1-C_5H_5) compounds of transition and nontransition metals. Cotton has provided a definitive perspective on initial developments in this area in several review articles[5,8,9] (of which one[8] is splendidly informal), in which the difficulties inherent in identifying the rearrangement pathway whereby a metal atom migrates around a cyclopentadienyl framework are explained. Thus differentiation between 1,2 and 1,3 movement of M in compounds (**1**) is a



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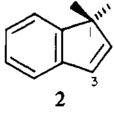

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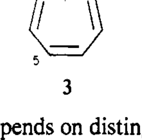

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nontrivial problem, the solution of which depends on distinguishing between NMR signals due to the two pairs of *chemically* (but not magnetically) equivalent nuclei in the C_5 ring. Various experiments directed toward this end have been documented,[10] all of which are consistent with, but do not prove, a 1,2-type rearrangement. Further indirect evidence to support this conclusion has been adduced from the nonrigid characteristics[11] of η^1-indenyl

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analogues (**2**) and by the inference using Forsen–Hoffman type spin-saturation measurements that **3** (M = $SnPh_3$) rearranges by a 1,5 ("molecular broad jump") rather than a "least-motion" shift[12] (the shifts in compounds **1** and **3** can alternatively be designated[13] as 5,1 and 7,4, respectively). An analogy between these phenomena and [1,5] thermal rearrangements described in orbital symmetry terms by Woodward and Hoffmann was also suggested some time ago, but substantive experimental data were not available.[14]

Our observation[15] of diastereotopically shifted ring-carbon resonances in the slow-limiting ^{13}C NMR spectrum of chlorobis(cyclopentadienyl)silane suggested a different approach to distinguishing 2,5 from 3,4 nuclei and led us to synthesize cyclopentadienes having chiral 1-silyl substituents. Assignment of temperature-dependent ^{13}C spectra for these latter has been put forward as more cogent evidence for a 1,2 (equivalent to 1,5) shift[16] although we had overlooked the fact that essentially the same argument had already been presented[17] in accounting for part of the dynamic behavior of $[Mo(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)(NO)(S_2CNBu\text{-}n_2)]^+$. Subsequently[18] we have shown that rearrangement of chiral silylcyclopentadienes occurs with retention of configuration at silicon, thereby exhibiting identical stereochemical characteristics to a sigmatropic [1,5] shift as defined[19] by Woodward and Hoffmann. This paper constitutes a fuller account of our results, providing inter alia substantiation of ^{13}C NMR assignments through comparison with computer-simulated data and a generalization of the mechanistic definition formulated for the silylcyclopentadienes to include the behavior of analogous germanium and tin compounds.

Experimental Section

Syntheses were conducted by using conventional high-vacuum methods as described earlier.[4,15,16,20] New compounds were purified by repeated trap-to-trap condensation and were definitively characterized by IR and mass spectroscopy as well as by the NMR spectra. The latter were measured as before, with Perkin-Elmer R32 (proton) or Nicolet TT-14 (carbon-13) spectrometers. Exchange-broadened proton-decoupled ^{13}C NMR spectra were simulated by using the DNMR3 program[21] modified to handle a five-site exchange model.

Synthesis of Compounds: Precursors. $MeSiHCl_2$ (**1**) was purchased and freed from HCl by vacuum fractionation, while reactions of $HSiCl_3$ with the appropriate organolithium reagent gave $n\text{-}BuSiHCl_2$, (**2**), and $Me_3SiCH_2SiHCl_2$, (**3**); physical and spectral data for the last two compounds were identical with those published previously.[21] We have already described[18] the synthesis of isopropylmethylchlorosilane (**4**). Methylphenylisopropyltin bromide (**6**) was prepared by the method of Gielen et al.;[22] similarly, the germanium analogue Me(Ph)(*i*-Pr)GeBr (**5**), bp 57–58 °C (0.1 mm) was isolated by successive Grignard alkylation of methyltrichlorogermane with phenyl- and isopropylmagnesium bromides in ethereal solution.

Conversion to Chiral $\eta^1\text{-}C_5H_5$ Derivatives. Reaction of the precursors (**1–6**) with potassium cyclopentadienide at −78 °C, either directly or in dry diethyl ether, afforded the corresponding cyclopentadienes (**7–12**). The following two experiments are typical: (A) Onto solid KC_5H_5 (from K metal, 0.30 g, 7.7 mmol and excess C_5H_6 monomer) was condensed $Me_3SiCH_2SiHCl_2$ (2.07 g, 11.07 mmol). After 75 min at −78 °C, volatile material was pumped (Hg diffusion) from the reaction vessel through traps at 0, −25, −78, and −196 °C. Unreacted **3** (0.77 g, 4.11 mmol) collected at −25 °C while the colorless liquid product was held at 0 °C and was refractionated to give pure (trimethylsilyl)methylchlorosilylcyclopentadiene (1.08 g, 5.02 mmol, 65.2%). (B) Compound **6** (3.07 g, 9.20 mmol) was allowed to react with excess KC_5H_5 in Et_2O (10 cm^3) at −78 °C for 60 min; removal of volatiles followed by extraction with dry hexane yielded liquid material from which sublimed [110 °C (10^{-2} mmHg)] colorless liquid (methylphenylisopropylstannyl)cyclopentadiene (1.85 g, 5.80 mmol, 63%) (**12**).

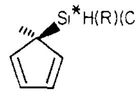
Table I. Precoalescence ^1H NMR Data[a]

compound	T/K	chemical shift/τ[b] H_{abcd}	H_x	H_y	H_p	H_q	H_r
7	213	3.18 3.21 3.27 3.37	6.34	5.91[c]	9.78		
8	213	3.21 3.28 3.46	6.36	6.27	9.36	9.36 8.86	
9	253	3.34 3.40 3.49	6.42	5.90	10.12	10.20	
10	233	3.46	6.57	6.35	8.91[d] 8.95[d] 8.98[d] 9.03[d] 10.26		8.72
11	213	3.18 3.35	5.79		8.63[d] 8.66[d] 8.68[d] 8.73[d] 9.76		8.45

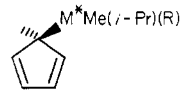
[a] Recorded in $CDCl_3$ solution throughout. [b] Proton environments are distinguished as follows: abcd, olefinic C_5-ring hydrogen atoms; x, aliphatic C_5-ring hydrogens; y, substituent Si–H hydrogens; p, substituent methyl hydrogens; q, substituent methylene hydrogens; r, substituent methyne hydrogens. [c] An apparent pentet due to coupling to H_a, H_b, and H_p where $J_{a(b)y}$ = 3.0 Hz, H_{py} = 3.0 Hz. [d] A pair of doublets due to a pair of anisochronous methyl groups each coupled to the methyne proton.

Results

Although synthesis of appropriate halogeno group 4 derivatives required several steps, reaction with cyclopentadienide anion occurred predictably to afford in good yield the corresponding cyclopentadienes **7–12**. These products are volatile, colorless liquids, like the related achiral compounds we have described[4,15,16,18,20] earlier; full IR and mass spectral data were recorded and were useful for characterization purposes but otherwise require no special comment.



7, R = Me
8, R = *n*-Bu
9, R = Me_3SiCH_2



10, M = Si, R = H
11, M = Ge, R = Ph
12, M = Sn, R = Ph

We begin by emphasizing that while each of the compounds **7–12** is chiral at the group 4 atom, all are racemic and will exhibit no chiroptical properties. Rather we are concerned with magnetic nonequivalence generated among chemically equivalent nuclei under the influence of the asymmetric center, leading to possible anisochronicity (diastereotopic shifts) in NMR spectra. Thus the familiar aa′bb′x array for the C_5 ring protons[7,20] will transform to an abcdx spin system, and the degeneracy of C^2, C^5 and of C^3, C^4 resonant frequencies may be lifted. Both of these effects are realized in the slow-limit NMR spectral data for **7–11**, which are summarized in Table I (^1H) and Table II (^{13}C measurements). With increasing temperature, resonances attributable to cyclopentadienyl ring nuclei progressively collapse and coalesce to an averaged chemical shift as has been observed for all related systems.[9] Temperature dependence in ^{13}C spectra has already

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Table II. Precoalescence ^{13}C NMR Data[a]

		chemical shift/ppm[b]		
compound	*T*/K	C^{2-5}	C^1	C^{other}
7	233	133.6 (96)[c] 132.7 (100) 131.8 (91) 130.3 (97)	51.1 (86)	−1.1[d]
8	218	133.7 (50) 132.6 (100) 129.9 (43)	50.6 (40)	25.6[e] 24.0[e] 20.1[e] 13.6[e]
9	223	133.5 (94) 132.7 (100) 132.3 (89) 130.9 (87)	52.2 (74)	2.2[f] 0.7[d]
10	233	133.4 (74) 132.7 (64) 130.6 (100) 130.3 (97)	47.6 (61)	18.7[g] 18.4[g] 13.5[h] −10.5[d]
11	213	134.1 (100) 133.3 (95) 132.1 (99) 131.4 (83)	48.4 (75)	19.1[g] 17.9[h] −11.5[d]

[a] $CDCl_3$ used as a solvent and internal reference throughout. [b] High frequency relative to δ 77.2 for $CDCl_3$ (central component of triplet). [c] Numbers in parentheses indicate relative intensities. [d] Substituent methyl carbon atom. [e] Substituent *n*-butyl carbon atoms. [f] Substituent methylene carbon atom. [g] Substituent isopropyl methyl carbon atom. [h] Substituent methyne carbon atom.

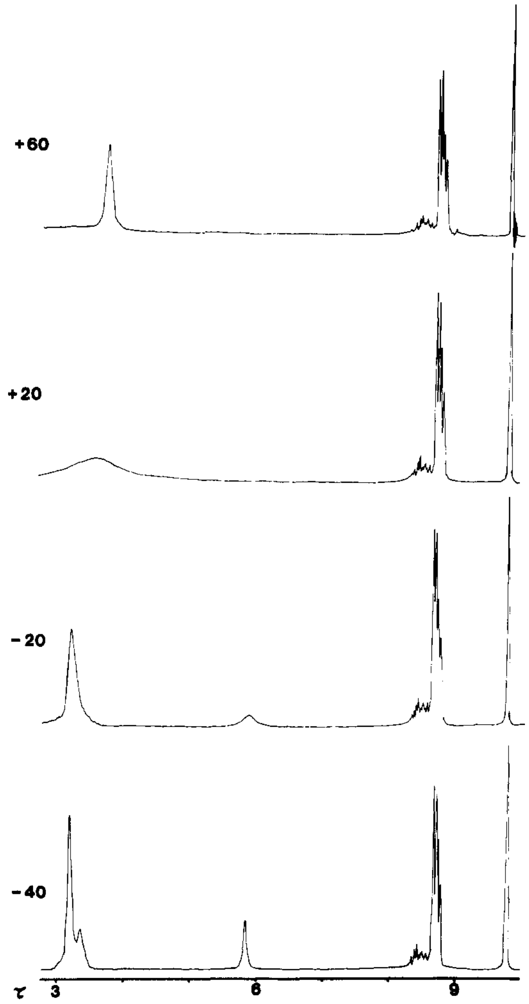


Figure 1. ^{1}H NMR spectra for compound **11** at various temperatures.

been illustrated for compounds **9** (Figure 2 of ref 16) and **10** (Figure 1 of ref 18); proton data for the germanium compound **11** at representative temperatures are here shown in Figure 1. The

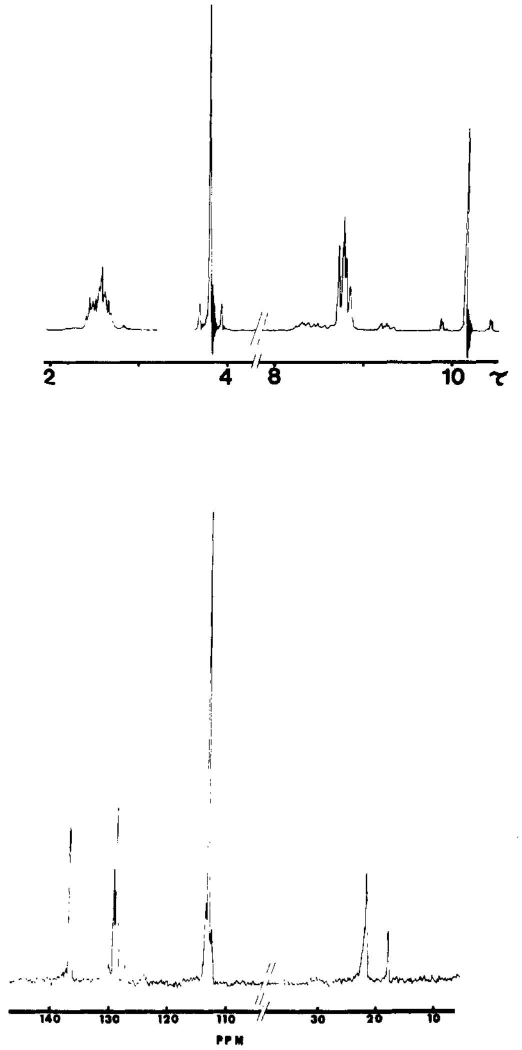
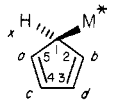


Figure 2. ^{1}H (top) and ^{13}C (bottom) NMR spectra for compound **12**.

^{1}H and ^{13}C spectra for the tin species are each fast limiting (fully coalesced) at all accessible temperatures (Figure 2); this is expected on the basis of earlier work,[1,8,9,23] which has established that a successive decrease in activation energy for the metallotropic process occurs down the group from silicon to tin.

Finally, we have used DNMR3 to simulate the coalescence of proton-decoupled ^{13}C NMR resonances for the silylcopentadienes; the results are illustrated in Figure 3 for compound **10**, calculated on the basis of each of the two alternative pathways for differential collapse[8-10] and correlating with the experimental spectra published earlier (ref 18, Figure 1). In the remainder of this section, in which the temperature dependence of the data will be described in terms of the assignments offered in the tables and by reference to the figures, ^{1}H spins are labeled abcdx and ^{13}C nuclei are numbered C^{1-5} as shown in **13**; the latter is arguably incorrect but has been hallowed by frequent use.[4,8-10]



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Dealing firstly with the proton spectra, at the slow limit a partly resolved unsymmetrical envelope at τ 3–3.5 accounts for the abcd (olefinic) multiplet while a singlet well separated to high field is due to the unique (x) hydrogen resonance. With increasing temperature the latter broadens and coalesces with the olefinic signal, in which for each compound differential collapse is dis-

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[23] Larrabee, R. B. *J. Organomet. Chem.* **1974**, *74*, 313.

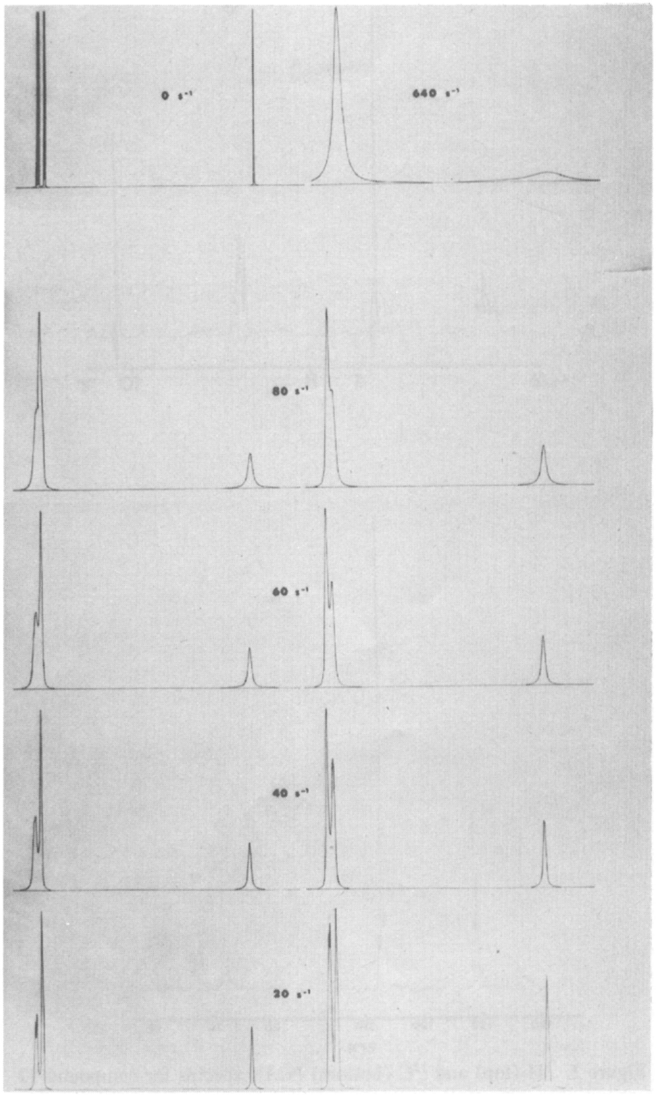

Figure 3. Computer-simulated ^{13}C NMR spectra for compound **10** for various rates of intramolecular exchange. The top line shapes simulate slow and fast exchange behavior while the remainder are calculated assuming (left-hand) 1,2 or (right-hand) 1,3 migratory pathways.

tinguishable, beginning with the upfield portion. Chemical shift differences in the low-field region are largest for the *n*-butylsilane (as shown in Figure 1 of ref 16), where coalescence of the two weaker resonances precedes that of the central component. This led us to propose[16] an assignment in terms of a relatively large diastereotopic shift (~0.2 ppm) between H_a and H_b, with a near-zero difference between H_c and H_d, which are a further bond away from the chiral silicon center. The observed changes lead progressively (e.g., Figure 1) to a single broad resonance at an averaged chemical shift, the line width of which narrows on further increasing the temperature toward an appearance paralleling that observed for the tin compound (**12**) (Figure 2A) for which the spectrum is fast limiting with $\tau_{av} = 3.81$ and J_{av} ($H-^{117,119}Sn$) = 22 Hz.

For the chloroalkylsilylcyclopentadienes (**7–9**), features attributable to substituent methyl and methylene groups (τ 8–10.5) appropriately showed no temperature dependence. By contrast, although in each case its chemical shift remained invarient near τ 6, changes in the multiplicity of the SiH resonance occurred which followed the coalescence behavior described above; thus a pentet structure, at −60 °C for the methyl compound (**7**), attributable to coincident $^3J(HH_{Me}) = {}^3J(HH_x) = 3.0$ Hz, transformed into a simple quartet ($J = 3.0$ Hz) at 30 °C as the H_x environment became averaged with those of the olefinic ring protons. As well as substituent methyl and silyl or multiplet phenyl proton lines, compounds **10–12** showed resonances attributable to the presence of the isopropyl group in the τ 8–9 range. The pattern is similar for all three systems and shows no temperature dependence (Figures 1 and 2A): four lines corresponding to two inequivalent methyl resonances each of which is split into a doublet by coupling to the single methyne (α) proton, with the latter giving rise to a complex multiplet slightly to lower field.

We turn now to the variable-temperature ^{13}C NMR measurements. In four compounds all five ring-carbon nuclei are differentiated at the slow limit (Table II; Figure 2 of ref 16, Figure 1 of ref 18), while in a fifth compound, **8**, two olefinic resonances (C^2 and C^5) are anisochronous but no splitting of the pair ($C^{3,4}$) more distant from the asymmetric silicon atom was resolved. Finally the tin compound (**12**) exhibits a single sharp line at an averaged chemical shift (δ 112.8, Figure 2B) with satellites due to $^1J_{av}(C-^{117,119}Sn) = 14$ Hz, again consistent with fast-limiting characteristics.

With increasing temperature the C^1 resonance near 50 ppm broadened and simultaneously differential collapse was observed in the olefinic region, as follows: (A) for each of the chloroalkylsilyl compounds **7–9**, the high and low frequency lines, separated by ~3 ppm, began to coalesce before the inner lines (e.g., Figure 2 of ref 16); (B) for compound **10**, the pair of lines to higher frequency (separation 0.7 ppm) collapsed together and much more rapidly than the low-frequency pair (separation 0.3 ppm; Figure 1 of ref 18), and the germane (**11**) showed similar behavior. We base our interpretation of these observations on the assumption that the magnitude of induced anisochronicity effects will be determined by distance from the inducing chiral center; i.e., here the $C^{2,5}$ pair is in each instance that showing the larger diastereotopic shift. It follows that (A) and (B) are entirely consistent with our earlier indirect assignments for ^{13}C NMR spectra of related achiral compounds, where we suggested[4] that in $C_5H_5SiR_3$ (R = H or Me) the $C^{2,5}$ resonance was that to higher frequency in the slow-limit spectrum, showing a diamagnetic shift to low frequency of $C^{3,4}$ on Cl substitution at Si (or Ge). The latter therefore also appears to exaggerate the diastereotopic shift between $C^{2,5}$, from 0.7 ppm in **10** to 3.8 ppm for **8**.

During the coalescence process referred to above the substituent ^{13}C resonances (due to Me, *n*-Bu, *i*-Pr, and Ph groups as appropriate) all remained unchanged. For compound **10** an unequivocal assignment of isopropyl carbon frequencies based on proton spin-coupling parameters has already been described in detail; the appropriate spectral range has also been illustrated, highlighting the observation of two diastereotopic methyl-carbon shifts.[18] Analogous splitting of the isopropyl β-carbon resonances was not resolved (at 15.09 MHz) in ^{13}C spectra of the germanium and tin (Figure 2B) compounds although for the former, at 62.9 MHz (Bruker MW250 spectrometer) and 22 °C, a small shift (0.08 ppm) was observable.

Discussion

Analysis of the dynamic behavior of cyclopentadienylmetal derivatives can be divided into three elements: molecularity (inter or intra), pathway (1,2 or 1,3), and mechanism. No information concerning the last of these has previously been available. The observation that the coalescence phenomenon results in averaging of spin-coupling constants[4,20,24] (between nuclei in the C_5 ring and those of the migratory substituent) as well as chemical shifts convincingly establishes intramolecularity.[9] It was recognized some time ago that differential collapse of the olefinic (aa′bb′) multiplet in ^1H NMR spectra precluded a random metallotropic rearrangement[8-10] and the balance of accumulated indirect evidence supports the earliest suggestion[25] of a 1,2 pathway. This conclusion is placed on a much more reliable basis by the results presented above, in which spectral assignments are based on the relative magnitude of the anisochronicity induced by chirality at the migratory center. Thus both in ^1H and ^{13}C NMR spectra, in every case, it is the pair of nuclei showing the larger diastereotopic effect which enter into coalescence first with increasing temperature.

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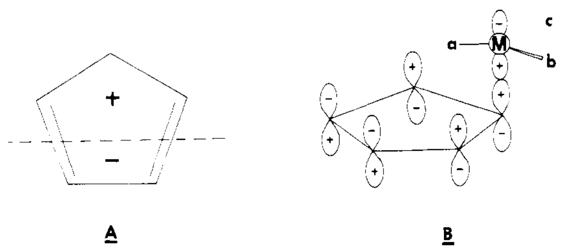

Figure 4. Symmetry properties of (A)Ψ_3 for the cyclopentadienyl radical and (B) metallocyclopentadiene rearrangement.

Interpretation of this observation in the same terms as the unsymmetrical collapse characterized for achiral analogous is in a sense approximate, because lifting of the degeneracies in 2,5 and 3,4 resonant frequencies complicates the algebraic description of the site exchange. The discrepancy will be minimal, since the diastereotopic shifts are much smaller than the frequency separation between nuclei in olefinic and in the 1-position, but to account for it exactly we have simulated ^{13}C data by using a five-site exchange program. From Figure 3, which shows the calculated parameters for compound **10**, it is clear that the 1,2 and 1,3 pathways will indeed generate distinguishable spectra: input data arbitrarily assigned the components of each pair but reversal (i.e., interchange of C^2 and C^5, and of C^3 and C^4) made no difference to the simulations. Comparison of the latter with observed spectra confirms a 1,2 pathway and gives $\Delta G^{\ddagger}_{300} = 61.1 \pm 1.3$ for compound **9** and 59.8 ± 2.7 for compound **10**; these activation parameters are fully consistent with our earlier results.[15] It also seems evident that our tentative analysis[4] of the high-frequency (olefinic) region of the ^{13}C NMR spectra for various silyl- and germylcyclopentadienes was correct and that in general where a,a′ and b,b′ resonances are distinguishable in ^1H NMR spectra the latter lie to lower field.

The fluxional behavior under discussion possesses the characteristics of a unimolecular reaction and may be regarded as a concerted sigmatropic[14,23] process. Its mechanism can be defined by the effect on stereochemistry at the migrating center. To test this we designed compounds **10–12**, incorporating an isopropyl substituent which is a so-called "diastereotopic group"; i.e., attachment to a chiral center renders the two methyls magnetically nonequivalent. It is plain that anisochronicity between the latter persists throughout the averaging of the C_5H_5 resonances in ^1H spectra for all three compounds (Table I; Figure 1) and also in the ^{13}C spectrum (ref 18) of **10**. This firmly establishes that for silicon, germanium, and tin compounds, rearrangement proceeds with retention of configuration at the metal atom.

Pathway and Mechanism. The stereochemistry of the thermal silaallylic rearrangement was first characterized some years ago by Slutsky and Kwart,[26] who showed it inter alia to be synonymous with racemization at optically active silicon. This establishes that the 1,3 sigmatropic migration is accompanied by inversion at Si. The present work implies that the related 1,5 shift occurs with retention of configuration. (The unlikely alternative is that the identification of a 1,2 pathway is wrong and that the dynamic behavior of silylcyclopentadienes is mechanistically unrelated to rearrangements in allylsilanes). We have already noted[18] that these processes thus possess characteristics identical with Woodward–Hoffmann [1,3] and [1,5] thermal rearrangements respectively. A further similarity lies in the energetic relationships to corresponding sigmatropic migration of carbon centers. Thus by contrast with the allylsilane situation, thermal fragmentation of appropriate systems occurs before the onset of carboallylic shifts;[26] likewise,[27] $\Delta G^{\ddagger}_{300} = 172.3$ kJ mol^{-1} for a rearrangement of methylcyclopentadiene which parallels the fluxional behavior of silylcyclopentadienes ($\Delta G^{\ddagger}_{300}$ in the range 50–60 kJ mol^{-1}). These differences may relate in part to the reduction in bond dissociation energy between C–C and C–Si but must also reflect changes in electronic structure of ground and/or transition states.

The frontier orbital Ψ_3 for the cyclopentadienyl radical has been predicted to have the form shown in Figure 4A from first-order perturbation theory,[28] on the basis that splitting of the Ψ_2,Ψ_3 pair will raise the energy of the molecular orbital having the largest number of nodes crossing formal double bonds. By qualitative development of the same argument, it seems plausible that in metallocyclopentadienes a ring orbital having corresponding symmetry properties contributes significantly to the interaction with the substituent group (Figure 4B). It has been suggested[26] that data for the sila–allyl shift indicate a preference for utilization of a 3p orbital in bridging the allylic structure with conservation of orbital symmetry. The metallocyclopentadiene rearrangement represented in these terms in Figure 4B is of course a simplistic representation but would be consistent with the observed stereochemistry (i.e., retention). While it is tempting to relate differences in orbital mixing (say[26] by involvement of nd_{z^2}) to the drop in activation energy between carbon shifts and those of lower members of group 4, this is as yet convincingly substantiated neither by calculations[29] nor by electron spectroscopy.[29c,30] Indeed, while the latter provides some evidence linking fluxional character to interaction between ring Π and (M–C)σ levels[30] as might be expected, certain[29c] of the former imply that corresponding overlap is developed between 1,3 (rather than 1,2) ring positions.

Finally we comment on the generality of these results, particularly in relation to η^1-C_5H_5 compounds of transition elements, where orbital availability at the migrating metal center will be modified considerably.[5,9] Our own efforts to prepare $(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)Fe(CO)(PPhMe_2)$ failed to afford a satisfactory product. We have subsequently learned[31] from J. W. Faller that in this complex anisochronicity among the phosphine methyl groups apparently persists in the fast-limiting ^1H NMR spectrum, although the compound was never obtained pure. Recently, however, Labinger reported[32] that in the related compound $(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_4Me)Fe(CO)(PF_2NMe_2)$ a diastereotopic splitting in the ^{19}F NMR spectrum is maintained during coalescence attributable to nondegenerate metallotropic shifts around the C_5H_4Me ring. These data suggest that 1,5 shifts with retention at the migratory center may also be characteristic of η^1-C_5H_5 transition-metal complexes. By contrast, it has been proposed[33] that the novel cycloheptatrienyl complex $(\eta^1\text{-}C_7H_7)Re(CO)_5$ is nonrigid via a 1,2 (equivalent to 1,7) pathway.

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Registry No. 1, 75-54-7; **2**, 4055-65-6; **3**, 18148-74-8; **4**, 2227-32-9; **5**, 80679-31-8; **6**, 21247-37-0; **7**, 80679-32-9; **8**, 80696-72-6; **9**, 80679-33-0; **10**, 80679-34-1; **11**, 80679-35-2; **12**, 80679-36-3; KC_5H_5, 30994-24-2.

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